United States Environmental Protection Agency

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Wastewater Treatment Fact Sheet: External Carbon Sources for Nitrogen Removal

DESCRIPTION

Discharge permits for publicly owned treatment works (POTWs) and industries often include effluent limits for nutrients, including nitrogen. Total maximum daily loads (TMDLs) for nutrients have and are being developed for many water bodies throughout the United States. The TMDLs and resultant waste load allocations to protect impaired water bodies have resulted in more stringent effluent limits for total nitrogen.

In order to achieve very low total nitrogen limits of less than 6 mg/l through biological denitrification, a readily biodegradable carbon source must be available for the denitrifying organisms to use. A supplemental external carbon source is often required when organic material in the wastewater has been oxidized. This is especially true in denitrification processes that are located after the aeration process such as post or second anoxic zone and denitrifying filters.

This fact sheet will provide information on external supplemental carbon sources to utility managers and operators of wastewater treatment facilities that have existing nitrogen permit limits or will be required to remove nitrogen in the future.

OVERVIEW

Bacteria utilize carbon as an energy source to drive metabolism as well as for the synthesis of new cellular material. Microorganisms obtain their carbon needs from organic compounds or from carbon dioxide. Heterotrophic microorganisms are able to utilize organic carbon sources while autotrophic organisms utilize carbon dioxide as a carbon source. When microorganisms utilize organic carbon as a substrate, energy is produced by the biochemical oxidation of organic carbon to carbon dioxide.

There are two major sources of organic carbon utilized in wastewater treatment operations. The sources are defined with respect to whether they originate within the influent wastewater entering the treatment facility or are provided as an external supplemental carbon source added to the treatment system. Carbon sources are termed ***external*** when the carbon substrate is sourced from outside the wastewater treatment process i.e., it is not derived from the influent wastewater or any onsite treatment processes at the treatment facility. External supplemental carbon sources are brought into the wastewater treatment process usually as pure compounds or high strength waste materials where concentrations can be as high as 1.5 g/L chemical oxygen demand (COD) to facilitate nutrient removal. ***Internal*** carbon sources refer to organic carbon substrates obtained either within the influent wastewater (as an organic wastewater load entering into the plant from the influent) or from accumulated materials stored within the cells also referred to as endogenous carbon sources.

CARBON AUGMENTATION FOR NITROGEN REMOVAL

Nitrogen removal involves the initial transformation of ammonia and organic nitrogen to nitrates via nitrification, and the subsequent elimination of nitrogen through denitrification. Because nitrification typically only occurs following carbonaceous biological oxygen demand (BOD) removal, the limiting factor for effective ddenitrification is often the absence of a readily biodegradable carbon source that can be used as an effective substrate by denitrifying bacteria during the denitrification process. Without the availability of a ready source of biodegradable carbon, denitrification will not occur, or will occur too slowly for sufficient nitrogen removal to occur.

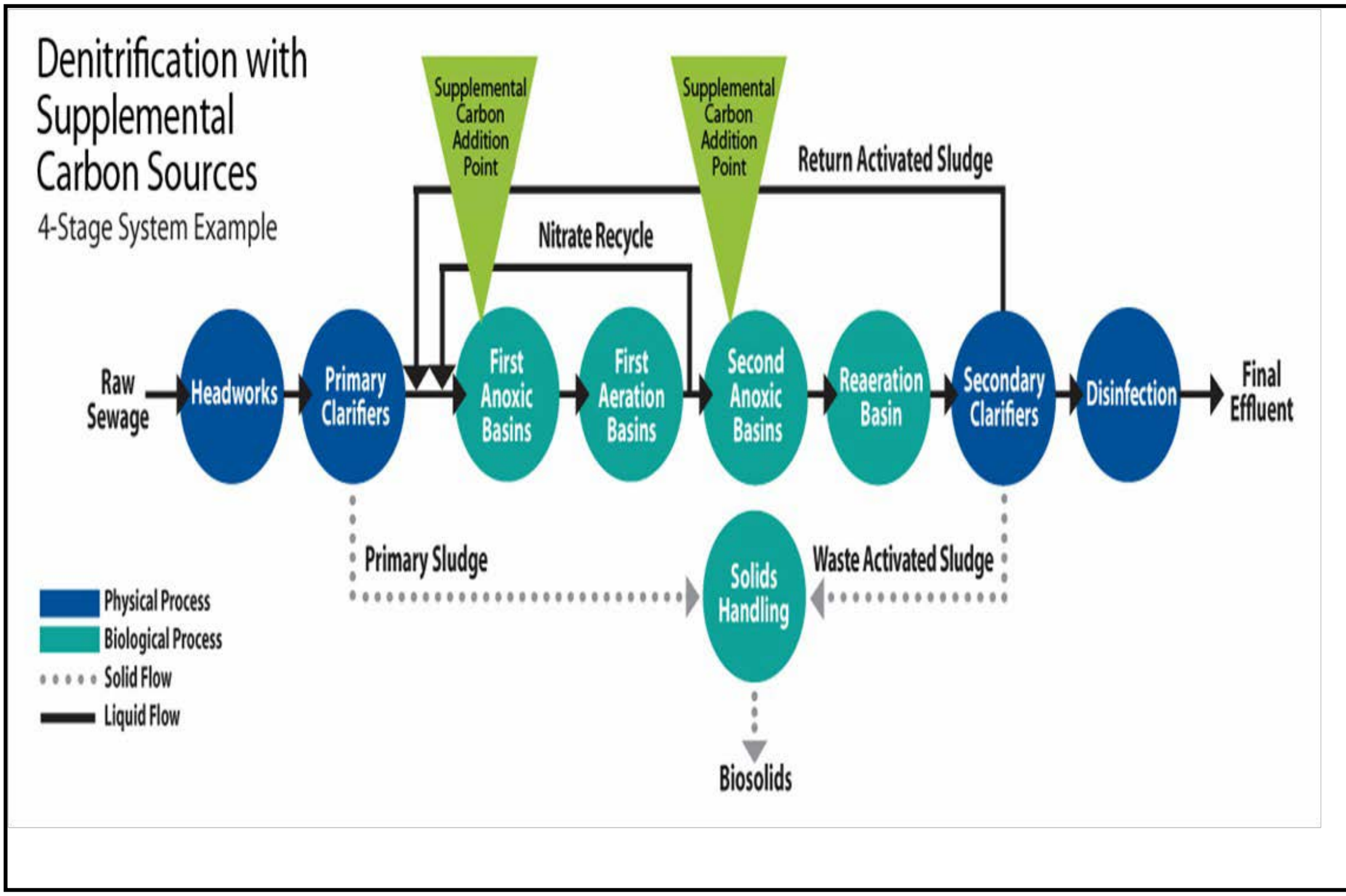

Figure 1: Illustration of Wastewater Treatment Process and Supplemental Carbon Feed Points

By using recycle schemes and step-feed processes, nitrates are brought into contact with sources of readily biodegradable carbon in the plant. Processes such as the Modified Ludzak-Ettinger (MLE) process enable contact between the nitrates formed at the back end of the wastewater treatment process and soluble COD generally found in the influent wastewater streams by recycling nitrate laden process flows to the head of the treatment system. However, in the MLE, step-feed and sequencing batch reactor (SBR) processes, a supplemental external carbon source might still be required to facilitate nitrate removal when internal carbon is not available in high enough concentrations (see Figure 1 for MLE and post anoxic zone processes common supplemental carbon feed points).

Denitrification processes that are located after the aeration process such as post or second anoxic zones and denitrifying filters will generally always need an external supplemental carbon source to be added, as almost all of the internal carbon sources have been utilized in the aeration process and only a very limited amount endogenous carbon is available for denitrification.

A wide range of carbon sources can be used to meet the soluble COD needs for denitrification. Commonly used sources of external carbon include methanol, ethanol, acetate, acetic acid, glycerol, molasses sugar water and proprietary formulations like MicroC™, a suite of carbon sources manufactured by Environmental Operating Solutions, Inc.

The choice of carbon source typically will depend on the evaluation of a number of product attributes, including: safety, cost, handling requirements, ease of use, materials compatibility, as well as kinetics and yield dynamics. The choice of a carbon source can have profound implications not just on the efficacy of nutrient removal, but also on plant and personnel safety, sludge yields, aeration adequacy, environmental sustainability, overall effluent quality and other factors. Tables 1 and 2 provide an overview of different carbon sources as well as a qualitative assessment of their ratings on a variety of attributes and product characteristics.

IMPORTANT FACTORS TO CONSIDER WHEN SELECTING AN EXTERNAL CARBON SOURCE

Safety

Safety is a very important consideration for carbon source selection. The use of external carbon sources such as methanol, acetic acid and ethanol for enhanced nutrient removal has expanded the scope of safety concerns in wastewater treatment facilities. The most significant concerns are that of flammability and explosion hazards associated with methanol and ethanol.

The levels of flammability associated with the carbon source selected will have an impact on the cost of the systems that will need to be put in place to ensure that the risk of fires and explosions are mitigated through compliance with applicable National Fire Protection Association (NFPA) fire and safety codes. Also, the hazards associated with handling these products will require Occupational Safety and Health Administration (OSHA) specific initial and annual recertification training of the plant operations staff. In 2006, a serious incident involving fatalities was recorded at a wastewater treatment plant using methanol as an external carbon source. This tragic incident brought to the forefront the need for safety considerations for flammable carbon sources, which include foam suppression systems, explosion proof storage, and spill containment.

Price Fluctuations

Many external carbon sources are derived from fossil fuel based raw materials. Significant price fluctuations in the methanol, ethanol, and acetic acid markets can have a huge impact on the prices of these carbon sources.

Agriculturally derived carbon sources such as molasses, glycerol, corn syrup, sucrose and MicroC™, tend to have more predictable and less volatile price profiles. In order to ensure that lifecycle costs associated with the external carbon system reflect the potential for significant price movements, especially with regards to fossil fuel based carbon sources, evaluations for carbon source selection should incorporate an analysis that incorporates historical price changes into the evaluative framework.

DOSAGE AND KINETIC CONSIDERATIONS

The dosage requirement refers to the amount of COD that is required to remove each unit of nitrate (i.e., the COD:N ratio, which is usually expressed as lbs COD/lbs NO_3-N removed). This ratio is affected by factors such as the nature of the carbon source, the species of biomass supported, the electron donor capacity of the carbon source, the solids retention time (SRT) of the treatment system and the sludge yields associated with bacterial species supported by the carbon source.

Kinetic considerations typically focus on the specific denitrification rates and the biomass growth rates associated with the carbon source. This is generally a function of the species of biomass that are selected for use in the treatment process when a carbon source is utilized. When methanol is used as a carbon source, methylotrophic denitrifying bacteria are selected for, resulting in a slower overall growth. Non methanol carbon sources such as glycerol, acetic acid, and the MicroC™ suite of products can be metabolized by the general heterotrophic bacterial populations found in the wastewater treatment process.

Methylotrophic biomasses are known to have very low growth rates. In colder temperatures, the growth rate is even lower, potentially leading to a reduced capacity for denitrification in the winter period

	Methanol	Ethanol	MicroCg™	MicroCglycerin™	56% Acetic Acid	30% Sodium Acetate
COD mg/L	1,200,000	1,650,000	670,000	1,016,000	577,000	222,480
Bulk Density lbs/gal.	6.6	6.6	10.2	9.92	9.09	9.8
Yield g COD/g COD	0.41	0.55	0.6	0.55	0.53	0.53
Total COD/N	4.82	6.36	6.45	6.36	6.09	6.09
Total dose gal substrate/ lb NO3N	0.48	0.46	1.15	0.77	1.19	3.09

Table 1: Product Characterization for Some External Carbon Sources

QUALITY CONTROL

Carbon sources are generally pure products (e.g., methanol, ethanol, MicroC™), unrefined wastes, or purified waste materials derived from a variety of industrial and agricultural processes. Some typical sources of external carbon include spent sugars from food and beverage manufacturing and glycerol from bio-diesel production. Generally, the costs of carbon sources derived from waste products tend to vary with the level of purity. However, given the processes from which these materials are derived, waste materials can contain impurities that could be problematic to the wastewater treatment process, pumping and handling and process kinetics. Such unrefined waste materials tend to have variable compositions, and this can have significant effects on the safety as well as the efficient functioning of the nutrient removal process.

When external carbon sources are applied for nutrient removal, especially in tertiary deep bed biological filters, it is important for the carbon source to have a consistent COD loading, given the fact that tertiary effluent systems have few downstream processes that are capable of handling significant COD breakthrough. Furthermore, variability in product quality can have a significant effect on the temperature vs. viscosity relationship, gelling and freezing point temperatures, phase separation, and presence of suspended solids and foreign material; all of which could impact the handling properties of the carbon source.

To further supplement this fact sheet, The Water Environment Research Foundation has published a detailed protocol to evaluate alternative external carbon sources for denitrification at full-scale wastewater treatment plants that provides in-depth information in evaluating carbon source (see the reference section below for more details).

	Alcohols		Acetate		Carbohydrates			Co-products	EOSi Products	
Product Attribute	Methanol	Ethanol	Acetic Acid*	Sodium Acetate**	Corn Syrup	Molasses	Sucrose Solutuion	Crude Glycerin	MicroCg	MicroCglycerin
Safety / Flammability	1	1	2	4	4	4	4	4	4	4
Price Volatility	2	2	2	2	3	3	3	2	3	3
Rate of Denitrification	2	4	4	4	3	3	3	3	3	4
Viscosity / Handling	4	4	4	3	1	1	1	2	4	4
Freezing Point	4	4	4	1	2	2	2	3	3	4
Product Stability	4	4	4	4	2	2	1	3	4	4
Supply Availability	4	4	4	4	4	4	4	2	4	3
Quality Control	4	4	4	4	4	3	3	1	4	4
Cost	4	3	1	1	1	2	2	3	2	3
Large body of technical literature	4	4	4	4	2	2	2	2	3	3

*56% solution **30% solution. Requires mixing

4 Very Good
3 Good
2 Fair
1 Poor

Table 2: External Carbon Sources and Evaluation of Some Common Attributes

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